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(54) Title: COMPOSITIONS

(57) Abstract: There is described a fuel composition comprising biodiesel and a surfactant, characterised in that the surfactant comprises a mixture of an alkanolamide, an alkoxylated alcohol and an alkoxylated fatty acid or a derivative thereof. More particularly there is described a fuel composition in which the diesel component is a mixture of biodiesel and petroleum diesel, e.g. up to 20 % v/v biodiesel. There is also described a method of running an internal combustion engine comprising the use of a fuel according to claim 1.

# COMPOSITIONS

This invention relates to a novel fuel composition and to methods of their preparation and use.

Diesel fuel is an important petroleum product and is depended upon for powering the engines of ships, trains, trucks, etc. Since petroleum is a non-renewable resource and because the burning of diesel in an internal combustion engine produces high levels of pollutants, especially particulates, much effort has gone into the development of alternative fuels from renewable sources.

Since the 1930's biodiesel fuel has been considered as an alternative to petroleum based diesel. In some cases vegetable oils have been added to petroleum diesel to try and at least mitigate some of the problems with petroleum diesel. Such vegetable oil may originate from a variety of sources, such as soybean oil, rape seed oil, palm oil and sunflower oil.

However, the use of biodiesel or petroleum diesel/biodiesel mixtures presents a number of difficulties. Biodiesel has a much higher cloud point (about 0°C) than petroleum diesel and also has a much higher pour point (about -2°C). Thus, the widespread use of biodiesel fuels does not appear practical until, *inter alia*, the low temperature viscosity issues of the fuel are addressed. Biodiesel fuels are also known to cause much more wear and tear on engines and have higher particulate emissions than conventional petroleum diesel fuel.

Attempts have been made to overcome these disadvantages by using emulsions of alcohols and vegetable oils, often including the use of a surfactant. However, these emulsions are not particularly stable at low temperatures and the alcohol has a tendency to absorb water.

We have now surprisingly found a fuel composition which overcomes or mitigates the problems of prior art fuels.

Thus according to the invention we provide a fuel composition comprising biodiesel and a surfactant, characterised in that the surfactant comprises a mixture of an alkanolamide, an alkoxylated alcohol and an alkoxylated fatty acid or a derivative thereof.

The diesel component of the fuel composition can comprise up to 100% v/v biodiesel. However, the diesel component is preferably a mixture of petroleum diesel and biodiesel. Such a mixture can comprise up to 20% v/v biodiesel, for example from 1 to 20% v/v, preferably from 5 to 20% v/v, more preferably from 10 to 20% v/v.

In a preferred embodiment the fuel composition also comprises an alcohol e.g. an alkanol, such as ethanol. When an alcohol is present the alcohol, e.g. ethanol, may be present in an amount of from 1 to 10% v/v, preferably 5 to 10% v/v and more preferably 1 to 3% v/v.

In the surfactant composition, the alkanolamide is preferably an ethanolamide and more preferably a diethanolamide. Especially preferred are the diethanolamides and particularly the super diethanolamides. By the term super diethanolamide we mean a diethanolamide in which the nitrogen is substituted by an alkyl substituent e.g. alkyl $C_5$ to $C_{20}$, preferably $C_8$ to $C_{18}$, more preferably $C_{10}$ to $C_{18}$. The most preferred diethanolamide is a $C_{18}$ substituent i.e. oleic diethanolamide. The term super amide normally refers to an amide derived by reaction of substantially stoichiometric proportions of diethanolamine with a fatty ester, typically a methyl or glyceryl ester.

There are three commercial routes to alkanolamides;

Acid + alkanolamine = alkanolamide + water

Plant or animal oil (triglyceride) + alkanolamine = alkanolamide+glycerol

Methyl ester + alkanolamine = alkanolamide + methanol

These are listed in order of increasing product quality. The route via the acid often uses an excess of alkanolamine to produce a product higher in amide than is obtainable from the acid if a stoichiometric ratio is used; these products are sometimes referred to as Kritchevsky amides.

The alkoxylated alcohol is preferably an ethoxylated alcohol. It is essential that the ethoxylated alcohol is an oil soluble alcohol. Therefore, alkanols are preferred and these may be primary, secondary or tertiary alkanols and especially primary alkanols. As the oil solubility of the alcohol may vary with the carbon chain length of the ethoxylated alkanol, the alkanol is preferably a $C_5$ to $C_{22}$ alkanol, more preferably $C_5$ to $C_{15}$ alkanol. The ethoxylated alcohol may comprise a mixture of alkanols or a mixture in which one alkanol will predominate. Thus, the most preferred alkanol is predominantly a $C_9$ to $C_{11}$ alkanol. In addition the degree of ethoxylation of the alcohol may be varied and the oil solubility will, generally, decrease with the increase in the degree of ethoxylation. It is preferred that the ethoxylate to alcohol ratio is greater than 2. More preferably, the ethoxylate to alcohol ratio is from between 1 and 10, preferably between 1 and 5, more preferably between 1 and 3 and especially between 2 and 3. A commercially available ethoxylated alcohol is especially preferred in which the ethoxylate to alcohol ratio is 2.75. Such an alcohol ethoxylate is available as NEODOL 91/2.5.

The fatty acid ethoxylate may comprise any conventionally known fatty acid ethoxylate or a derivative thereof. Thus the fatty acid ethoxylate may be derived from a fatty acid having from 8 to 20 carbon atoms, preferably from 10 to 18. The fatty acid may be a saturated or unsaturated fat. By the term "alkoxylated fatty acid or a derivative thereof we mean a derivative of the acid, for example, an ester e.g. an alkyl ester. The most preferred fatty acid is an unsaturated fatty acid and especially $C_{18}$ oleic acid or a derivative thereof, such as an oleate ester, e.g. an alkyl $C_1$ to $C_{10}$

oleate. Derivatives which may be mentioned include an ethyl oleate or a methyl oleate. In one embodiment of the invention, when ethanol is present then the fatty acid is greater than $C_{15}$ and especially oleic.

The degree of ethoxylation is chosen to optimise performance in the blend with the other two selected surfactants and may be from 1 to 20, but more preferably from 5 to 18. A suitable product within this range would be, for example that derived from the addition of 7 molecules of ethylene oxide to 1 mole of oleic acid.

The preferred additive of this invention is a non-ionic surfactant and preferably a blend of surfactants. It is a preferred feature of this invention that the surfactants be selected by their nature and concentration that the additive (as well as any water or other non-fuel liquid present) be solubilised within the fuel. For this purpose it is convenient to have regard to the hydrophilic-lipophilic balance (HLB) of the surfactant, the value being calculated according to the expression.

$$HLB = \frac{\text{mol. wt of hydrophilic chain x 20}}{\text{total mol. wt}}$$

The values will depend on the length of the hydrophilic chain, typically an ethoxylate chain. The length of the chain will increase the extent of solubilisation because of a greater ability to solubilise.

As with the compositions described in WO98/17745, a blend of surfactants is preferred, preferably by selecting one with an HLB appropriate to the fuel, say 10 to 18 for hydrocarbon fuel, most preferably 13. In the case of an alcohol the HLB value of the surfactant is between 3 and 7, most preferably about 4.

The invention has the ability to unify the HLB requirements of any liquid fuel which in turn allows for one dose to be used in any fuel from C5 carbon chains up. The benefit being the amount of treatment directly related to the co-solvency ability.

Preferably the ethoxylate of the fatty acid makes up about 25% by volume of the additive and further preferably the alcohol ethoxylate comprises 50% by volume of the additive.

An additive of the invention may be added to a hydrocarbon fuel, e.g. diesel, petrol or alcohol, such as ethanol which may or may not be contaminated with water. The invention is seen to particularly good effect when added to synthetic fuels based on low fraction oils.

The presence of the additive of the invention ensures that the fuel composition forms a consistent stable homogenous composition and creates a monolayer simultaneously a result of which leads to a better more complete burn which reduces pollution and increases miles per gallon.

The concentration of the additive in the fuel can be very low, typically the additive to fuel ratio may be of the order of 0.5 – 50:1200, preferably about 0.5-50:1000, more preferably 1-30:1000 and most preferably 30:1000. There appears to be no technical or economic benefit in adding more unless a co-solvent dual action is required, when the priority will be dosage against performance. In the aforementioned ratios the fuel is considered to comprise the sum of any petroleum diesel, biodiesel and alcohol present in the composition.

We also provide a method of running an engine adapted to use a diesel-based fuel, comprising adding to the petroleum diesel and biodiesel mixture a miscible additive selected to solubilise the fuel and the additive so eliminating the deposit of by-products formed during the combustion of the fuel.

CLAIMS

1. A fuel composition comprising biodiesel and a surfactant, characterised in that the surfactant comprises a mixture of an alkanolamide, an alkoxylated alcohol and an alkoxylated fatty acid or a derivative thereof.

2. A fuel composition according to claim 1 characterised in that the diesel component is a mixture of biodiesel and petroleum diesel.

3. A fuel composition according to Claim 1 characterised in that the fuel composition comprise up to 20% v/v biodiesel.

4. A fuel composition according to Claim 1 characterised in that a non-alkoxylated alcohol is also present.

5. A fuel composition according to Claim 4 characterised in that the alcohol is an alkanol.

6. A fuel composition according to Claim 5 characterised in that the alkanol is ethanol.

7. A fuel composition according to Claim 1 characterised in that the fuel composition comprise from 1 to 20% v/v of a non-alkoxylated alcohol.

8. A fuel composition according to Claim 4 characterised in that the amount of alcohol present is from 1 to 10% v/v.

9. A fuel composition according to Claim 8 characterised in that the amount of alcohol present is from 5 to 10% v/v.

10. A fuel composition according to Claim 1 characterised in that the alkanolamide is an ethanolamide

11. A fuel composition according to Claim 1 characterised in that the alkanolamide is a diethanolamide.

12. A fuel composition according to Claim 11 characterised in that the diethanolamides are super diethanolamides.

13. A fuel composition according to Claim 11 characterised in that the nitrogen in the diethanolamide is substituted by an alkyl $C_5$ to $C_{20}$ substituent.

14. A fuel composition according to Claim 13 characterised in that the diethanolamide is substituted by an alkyl $C_8$ to $C_{18}$ substituent.

15. A fuel composition according to Claim 14 characterised in that the diethanolamide is substituted by an alkyl $C_{10}$ to $C_{18}$ substituent.

16. A fuel composition according to Claim 15 characterised in that the diethanolamide is a lauryl diethanolamide.

17. A fuel composition according to claim 15 characterised in that the alkyl substituent is an unsaturated substituent.

18. A fuel composition according to claim 17 characterised in that the diethanolamide is oleic diethanolamide.

19. A fuel composition according to Claim 1 characterised in that the alkoxylated alcohol is an ethoxylated alcohol.

20. A fuel composition according to Claim 19 characterised in that the ethoxylated alcohol is an oil soluble alcohol.

21. A fuel composition according to Claim 19 characterised in that the ethoxylated alcohol is an ethoxylated alkanol.

22. A fuel composition according to Claim 21 characterised in that the ethoxylated alcohol is a primary alkanol.

23. A fuel composition according to Claim 1 characterised in that the alkanol is $C_5$ to $C_{22}$ alkanol.

24. A fuel composition according to Claim 21 characterised in that the ethoxylated alcohol comprises a mixture of alkanols in which one alkanol predominates.

25. A fuel composition according to Claim 21 characterised in that the predominate alkanol is a $C_9$ to $C_{11}$ alkanol.

26. A fuel composition according to Claim 25 characterised in that the ethoxylate to alcohol ratio is from between 1 and 10.

27. A fuel composition according to Claim 26 characterised in that the ethoxylate to alcohol ratio is from between 1 and 5.

28. A fuel composition according to Claim 27 characterised in that the ethoxylate to alcohol ratio is from between 2 and 3.

29. A fuel composition according to Claim 28 characterised in that the ethoxylate to alcohol ratio is 2.75.

30. A fuel composition according to Claim 29 characterised in that the ethoxylated alcohol is NEODOL 91/2.5.

31. A fuel composition according to Claim 1 characterised in that the fatty acid group is a $C_8$ to $C_{20}$ fatty acid or a derivative thereof.

32. A fuel composition according to Claim 31 characterised in that the fatty acid group is a $C_{10}$ to $C_{18}$ fatty acid or a derivative thereof.

33. A fuel composition according to Claim 32 characterised in that the fatty acid group is a $C_{14}$ fatty acid (myristic acid) or a derivative thereof.

34. A fuel composition according to claim 31 characterised in that the fatty acid is an unsaturated fatty acid or a derivative thereof.

35. A fuel composition according to claim 4 characterised in that the fatty acid is oleic acid or a derivative thereof.

36. A fuel composition according to Claim 1 characterised in that the composition comprises 25% v/v of the fatty acid ethoxylate or a derivative thereof.

37. A fuel composition according to Claim 1 characterised in that the composition comprises 50% v/v of the alcohol ethoxylate.

38. A fuel composition according to claim 1 characterised in that the surfactant additive to fuel ratio is from 0.5:1200 to 50:1000.

39. A method of running an internal combustion engine comprising the use of a fuel according to claim 1.

40. A fuel composition substantially as described with reference to the accompanying examples.

41. The use of oleic acid or a derivative thereof in the manufacture of a fuel composition according to claim 1.

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 01/00749

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10L1/02 C10L1/14 C10L10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 18 July 2001 | 25/07/2001 |

| Name and mailing address of the ISA | Authorized officer |
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| European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31–70) 340–2040, Tx. 31 651 epo nl,<br>Fax (+31–70) 340–3016 | De La Morinerie, B |

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Information on patent family members

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